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ALKYLATION AND POLYMERIZATION OF HYDROCARBONS WITH THE AID OF MOLECULAR COMPOUNDS OF BORON FLUORIDE WITH PHOSPHORIC ACIDS

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[The reactions described here are applied in the synthesis of high-octane fuel components and gasolines (isoheptanes and isooctanes). Another application is in the synthesis of special lubricating oils.]

In our work, studies were conducted on boron fluoride and its molecular compounds with organic oxygen-containing compounds and phosphoric acids.

Molecular compounds of boron fluoride with orthophosphoric, pyrophosphoric and metaphosphoric acids are vigorous catalysts of the reactions of alkylation and polymerization.

The alkylation of isobutane with propene and butenes at atmospheric pressure takes place slowly at 20°, and with a considerable velocity at 100° C, when the gaseous mixture is passed through the liquid catalyst or activated carbon which has been moistened with the catalyst. With other known catalysts (sulfuric acid, aluminum chloride) alkylation does not take place under analogous conditions. When isobutane is alkylated with propene and butene in the liquid phase under 4-5 atmospheres pressure at a temperature of 20° C and the ratio of paraffin to olefin is 3:1, the yield reaches 70-80%, and 80% of the product obtained boils away between 40° and 225°. Under the same experimental conditions, alkylation with sulfuric acid produces a yield of 7%.

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During the operation, molecular compounds of boron fluoride with phosphoric acids, when used as catalysts, are not poisoned and can work for an unlimited time, since acidic esters, which are formed as a result of the absorption of unsaturated hydrocarbons, are themselves vigorous catalysts of alkylation in combination with boron fluoride.

Molecular compounds of boron fluoride with phosphoric acids bring about the polymerization of ethylene, propene, and normal butenes at atmospheric pressure and temperatures of 50-100° when olefins are passed over activated carbon which is moistened with one of these compounds.

The products obtained as a result of this type of polymerization contain a greater amount of high boiling fractions than products of polymerization with orthophosphoric acid. In this connection it would be more expedient to test the molecular compounds of boron fluoride with phosphoric acids with a view of obtaining lubricating oils than of obtaining polymerized gasolines.

The catalysts which have been well known up to the present (phosphoric and sulfuric acids, aluminum chloride, etc.) bring about the polymerization of ethylene, propene, and n-butenes at 100° and atmospheric pressure when the latter substances are passed through a column containing the catalyst.

Boron fluoride and its molecular compounds with organic oxygen-containing compounds are less active than compounds of boron fluoride with phosphoric acid.

For example, the compound of boron fluoride with diethyl ether causes the polymerization at atmospheric pressure of isobutylene alone and does not polymerize normal butenes, while in reactions of the alkylation of isobutene it is not very active.

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